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Mechanism of the interaction of CO_2 and humidity with primary amino group systems for room temperature CO_2 sensors

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Abstract

The use of primary amino groups as receptors to detect CO_2 is promising because of their ability to perform reversible acid-base-reactions. In contrast to other sensitive materials using this effect, evaluable signals can be obtained even at ambient temperature. The effect discussed for most of the previously used sensing layers is the formation of bicarbonate species, which needs H_2O as well as an increased temperature. The use of primary amino groups and work function readout appears to be dominated by another reaction, the reversible formation of carbamate, which does not require any water presence and, in addition to that, is more efficient at lower temperatures. To confirm this hypothesis, IR-, Raman-, XPS- and NMR-spectroscopy were used.

Keywords: CO_2, carbamate, bicarbonate, room temperature, primary amino groups

1. Introduction

In recent years, various sensitive materials have been investigated for the use in mass sensitive and capacitive CO_2-sensors based on amino groups, which are contained in monomeric amines [1], polymeric amines [2] and modified silicates [3]. Drawbacks of these sensors are their long response time, the poor reversibility and sensitivity, a high cross-sensitivity to humidity as well as a limited long term-stability. Additionally, these materials often had to be operated at elevated temperatures (50-70°C) in order to reduce the cross-sensitivity to humidity as well as to generate detectable CO_2-signals, which can be explained by an acid-base-reaction.

Besides their usage in GasFET devices, the change of the work function provides information for a better understanding of the interaction of CO_2 with primary amino groups. Therefore, a change in mass or capacity is not required, as the work function is directly related to the gas adsorption. In addition to the advantage of the free choice of the sensitive materials, it is possible to operate the sensor at room temperature with high sensitivities [4]. As a result, the energy consumption is low and future applications are conceivable for small low-cost sensors.

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2. Experimental

In order to read out the change of work function, the Kelvin method is used. Gas measurements are carried out in synthetic wet air (40% relative humidity (r.h.), room temperature) using a base concentration of 400 ppm CO_2 (background in atmosphere) increasing up to 4000 ppm CO_2. IR spectroscopic measurements are conducted under vacuum conditions to avoid objectionable water peaks. Raman-, XPS-, NMR-spectroscopy are applied under normal atmosphere. The sensitive layers were intermediately stored under normal laboratory atmosphere (40% r.h., room temperature) in plastic boxes.

High quality Al_2O_3-ceramics (99.6%), covered with sputtered gold, serve as substrates for all types of these sensor materials. On the top of this electrode the gas sensitive material (heteropolysiloxane) is applied by means of spin-coating. The sensitive coating is manufactured via sol-gel processing of alkoxysilane precursors.

The investigated sensitive material is a heteropolysiloxane containing AMO (3-Aminopropyltrimethoxysilane) and PTMS (Propyltrimethoxysilane) in a mass ratio of 70:30. By the addition of PTMS a volitional hydrophobization of the hydrophilic AMO is reached due to an increased number of non-polar-groups in the material system. After the spin-coating-process the sensitive layers are temporarily stored under room air for two hours in order to allow the evaporation of solvents and, therefore, to reach a gel state. The sol-gel condensation is then further executed in N_2-atmosphere for 16 h under 120°C. The tempering removes the rest of H_2O and alcohol and leads to the formation of a solid state sensitive layer.

3. Results

3.1. Investigation of heteropolysiloxanes with Kelvin probe measurements

Immediately after manufacturing of the sensitive layers, a high sensitivity to CO_2 beginning with 400 ppm CO_2-background can be observed with Kelvin probe measurements. There seems to exist no major difference between the work function response to CO_2 in dry (0% r.h.) or in wet synthetic air (40% r.h.), both being 15-20 mV at exposure to 4000 ppm CO2 (Fig. 1(a)). However, there is a stronger drift of the baseline under wet conditions compared to dry air which shows that humidity leads to an ongoing change in the sensitive layer. Beyond that, one can detect a still higher drift during 4000 ppm CO_2-admission which indicates, that higher CO_2-concentrations associated with humidity cause a further change in the chemical layer.

With increasing time a decrease of the CO_2-response can be observed that finally reaches a stable state after some months (Fig. 1(b)). Between the measurements the samples are stored in normal atmosphere and room temperature and, consequently, they have contact with humidity and CO_2. Even after several months the stable response demonstrates the chemical stability of AMO/PTMS and the adjustment of the chemical equilibrium. A measurement with a seven month old sample shows an increase in the CO_2-response under dry conditions (Fig. 1(c)).

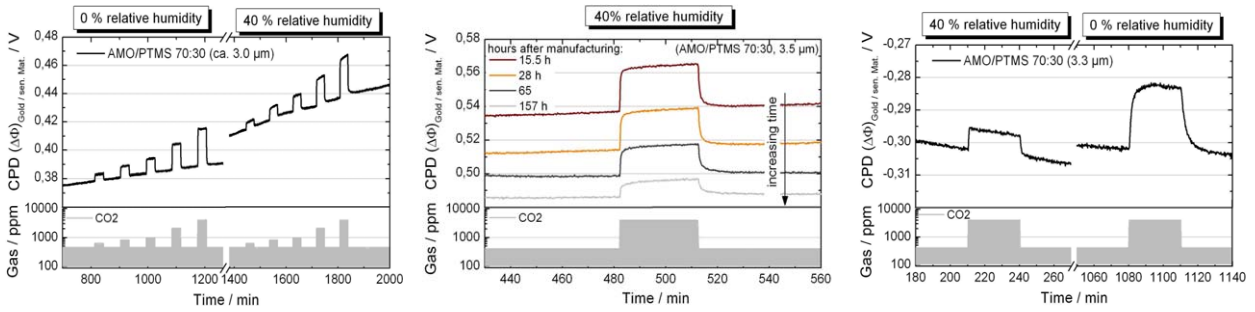

Fig. 1. Response of a AMO/PTMS thickness layer at 27°C (a) directly after manufacturing from 400 ppm CO_2 up to different CO_2-concentrations (b) over time after manufacturing from 400 ppm CO_2 up to 4000 ppm CO_2 at 40% r.h. (c) 7 month after manufacturing.

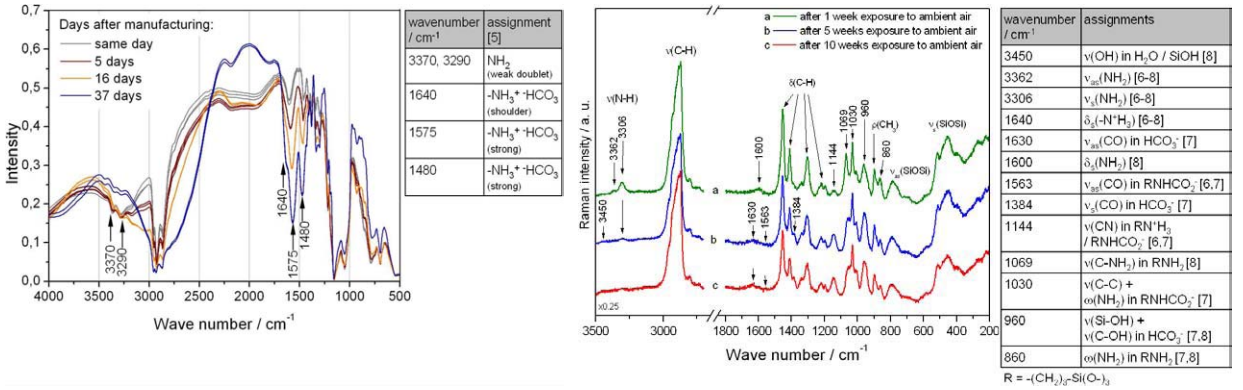

Fig. 2. (a) Dependence of IR-Spectra of an AMO/PTMS thick film on time (27°C; during measurement: vacuum; between measurements: stored in normal atmosphere); (b) Dependence of Micro-Raman-Spectra of an AMO/PTMS thick film on time (27°C, normal atmosphere).

3.2. Analyses of formed species with IR-, Raman-, NMR- and XPS-spectroscopy

The IR spectroscopic analysis (Fig. 2(a)) shows that the sensitive layers form ammonia ions (NH_3^+) and hydrogencarbonate (HCO_3^-) in the time span after the manufacturing process and are thus reducing the amount of primary reactive amino groups (RNH_2, R = moiety molecule) of the heteropolysiloxane. These species are characteristic for the formation of bicarbonate which needs H_2O. After two months a further change cannot be established and therefore the equilibrium is reached. The XPS-spectroscopy also shows (N 1s line) that the amount of C-N groups of AMO decreases and in exchange charged N^+ is built.

The Raman spectroscopy confirms the generation of hydrogencarbonate groups, as it can be seen in Fig. 2(b) with the vibrational bands at 1630 (ν_{as}(CO) in HCO_3^-), 1384 (ν_s(CO) in HCO_3^-) and 960 cm^{-1} (ν(C-OH) in HCO_3^-) [6-8]. Moreover, the Raman spectroscopy asserts that the primary amino groups (NH_2) decrease in the course of time as can be seen from the intensity decrease of the bands located at about 3300 cm^{-1} (ν(NH_2)) and 1069 cm^{-1}(ν(C-NH_2)). However, the Raman spectroscopy indicates the formation of another moiety, namely carbamate, which has its characteristic lines at 1144 (ν(CN) in RN^+H_3 / $RNHCO_2^-$) and 1563 cm^{-1} (ν_{as}(CO) in $RNHCO_2^-$), the latter being very weak [6-8]. The peaks of carbamate increase in the course of time as well as those of bicarbonate.

In order to ascertain the formation of carbamate, a solid state ^{13}C-NMR spectroscopy analysis was executed. In the spectrum (Fig. 3(a)), a peak at the position 164.6 ppm can be discovered, which is characteristic for a carbonyl group. According to Weng et al. [7], this peak could indicate the presence of carbamate, which is shifted of 2-3 ppm towards low field compared to those of ammonium bicarbonate and ammonium carbonate. Besides, all characteristic peaks for AMO and PTMS can be observed at their characteristic positions as one can see in Fig. 3(a). Furthermore, it has to be added that with all used spectroscopic methods no carbonate - which can be formed from bicarbonate per change of the pH-value - could be distinctly observed.

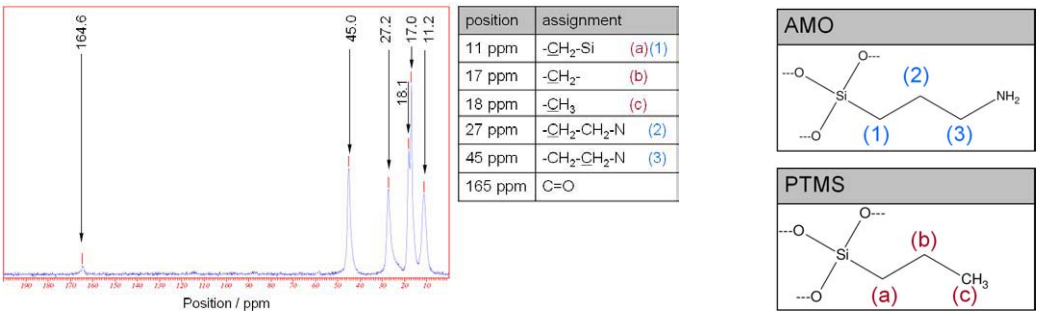

Fig. 3. (a) NMR-spectroscopy of a AMO/PTMS layer under normal atmosphere (10 weeks old sample); (b) Schema of AMO and PTMS.

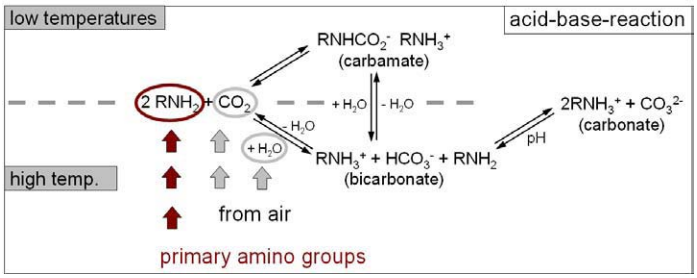

Fig. 4. Possible reaction paths of CO_2 with primary amino groups.

4. Discussion

Kelvin probe measurements show, that after the manufacturing process CO_2 can react with the primary amino groups of AMO in dry as well as in wet synthetic air, respectively. Besides, stronger drift of the contact potential difference (CPD) indicates a slow generation of species over time which increases with a growing concentration of humidity and CO_2. With the XPS-spectroscopy a decrease of the primary amino groups and an increase of ammonium moieties have been discovered. IR and Raman spectroscopy show that bicarbonate is built, which requires water (Fig. 4). Both, the high sensitivity to CO_2 of a fresh manufactured (and therefore waterless) layer as well as the higher response of a month old layer in dry air leads to the assumption that a carbamate moiety is formed, which is waterless and whose formation is more efficient at lower temperatures (Fig. 4). A direct transformation of bicarbonate into carbamate involving a separation of H_2O is also conceivable. The hypothesis of built carbamate as sensing reaction to the presence of CO_2 is confirmed by Raman- and NMR-spectroscopy which show both signals that are undoubtedly to be assigned to that moiety. The generation of carbonate could not be verified.

5. Conclusion

The better understanding of primary amino group systems with CO_2 and humidity is a highly interesting field for ambient solid state CO_2-sensors. This work takes a step forward into this area, as the formation of carbamate or a conversion of bicarbonate into carbamate takes place at room temperature. Therefore, sensitive layers can be systematically modified to increase the formation of this species (increase of hydrophobization or adjoining primary amino groups).

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